MATHCAD FILE FOR SIMULATION OF CATHODIC STRIPPING REACTION OF SECOND ORDER, ASSOCIATED WITH ADSORPTION OF THE LIGANS-CALCULATION FILE IN SQUARE WAVE VOLTAMMETRY

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Abstract

We provide the readers entire >MATHCAD working sheet for simulation of square wave voltammograms of simple Cathodic Stripping mechanism of second order that is coupled with the adsorption of reacting ligand. The simulation file contains all parameters for calculating SW voltammograms of this complex mechanism under conditions of square-wave voltammetry. Model is suitable to study the features of quasireversible electrode systems of many metal-ligand complexes and metal-drug complexes.

Catodna Striping r-ja od I red so atsorpcija na ligandot

$L^{2}(aq) = L^{2}(ads) + Hg(s) = HgL(s) + 2e$- (Rezultatite se objaveni vo Anal. Chim. Acta)

Cathodic Stripping reaction with Adsorption of reacting Ligand of Second Order in SWV

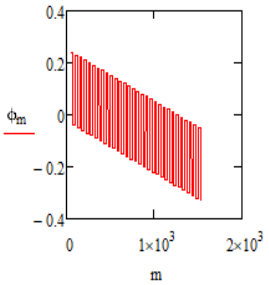
Kvazireverzibilna reakcija

$\Delta E := 0.3 \quad f := 10 \quad d := \frac{1}{50 \cdot f} \quad dE := 0.01 \quad Esw := 0.14 \quad t := 0.1 \quad s := 1 .. \frac{t}{d} \quad m := \frac{t}{d} + 1 .. \frac{\Delta E}{dE} \cdot 50 + \frac{t}{d} \quad Es := 0.1$

ΔE-potencijalen interval, DE = Ef-Es, Ef-kraen, Es-poceten potencijal
dE-potencijalen inkriment
t-vreme na akumulacija
d-vremenski inkriment

$$\phi_m := Es + Esw - \left[\left(ceil\left(\frac{m - \frac{t}{d}}{25} \cdot \frac{1}{2} \right) \cdot dE + if\left(\frac{ceil\left(\frac{m - \frac{t}{d}}{25} \right)}{2} = ceil\left(\frac{m - \frac{t}{d}}{25} \cdot \frac{1}{2} \right), 1, -1 \right) \cdot Esw + Esw \right) - dE \right]$$

$j := 5 .. 5$



$F := 96500 \quad n := 2 \quad R := 8.314 \quad T := 298.15 \quad Ks := 0.316 \quad Kads := 100 \quad D := 5 \cdot 10^{-6} \quad a := \sqrt{D} \cdot Kads \quad rs := 1$

Ks-standardna redoks konstanta na brzinata (s^{-1})
Kads-konstanta na atsorpcija (linearna atsorpcija) na ligandot (cm^{-1})
a-pomosen atsorpciski parametar ($s^{-1/2}$)
rs = 1 cm-pomosna konstanta

Ks = 0.316

$\Phi_m := n \cdot \frac{F}{R \cdot T} \cdot \phi_m \quad \rho := \frac{a}{\sqrt{f \cdot rs}} \quad \Phi ac := n \cdot \frac{F}{R \cdot T} \cdot Es \quad \alpha := 0.5 \quad \lambda := \frac{Ks \cdot rs}{\sqrt{f \cdot D}} \quad \gamma := \sqrt{\frac{D}{f}} \cdot \frac{1}{rs}$

$C := 0.1$

(Kads) = 100

ρ-bezdimenzionalen atsorpciski parametar (ovoj parametar vistinski go kontrolira efektt na atsorpcija vrz voltametriskiot odgovor)
λ-kineticki parametar
γ-difuziski parametar
Ovie se najvaznite parametri

$\log(\lambda) = 1.65$

$k := 1 .. \frac{\Delta E}{dE} \cdot 50 + \frac{t}{d} \quad R_k := e^{(a^2) \cdot k \cdot d} \cdot (1 - erf(a \cdot \sqrt{k \cdot d})) - e^{(a^2) \cdot (k-1) \cdot d} \cdot [1 - erf[\sqrt{(k-1) \cdot d} \cdot a]] \quad S_k := \sqrt{k} - \sqrt{k-1}$

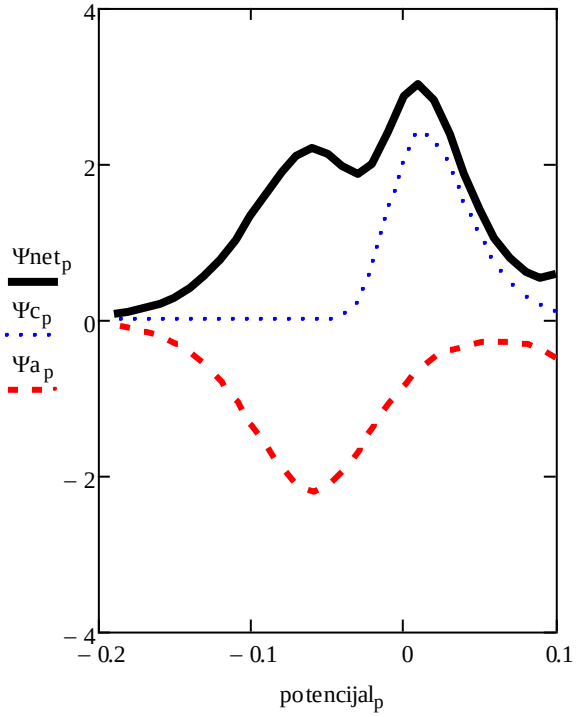
$x := 0.001$

$\Psi_1 := root\left[x - (\lambda) \cdot e^{-\alpha \cdot \Phi_1} \cdot \left[\left(\frac{-\gamma}{100}\right) - e^{\Phi_1} \cdot C \cdot \left[1 - e^{\left(\frac{\rho^2 \cdot 1}{50}\right)} \cdot \left(1 - erf\left(\rho \cdot \sqrt{\frac{1}{50}}\right)\right) + \left(\frac{2 \cdot S_1}{\sqrt{\pi}} + \frac{\sqrt{50}}{\rho} \cdot R_1\right)\right]^2\right], x\right]$

$\Psi_s := root\left[x - \lambda \cdot e^{-\alpha \cdot \Phi ac} \cdot \left[\left(\frac{-\gamma}{100}\right) \cdot \left(x + \sum_{i=1}^{s-1} \Psi_i\right) - e^{\Phi ac} \cdot C \cdot \left[1 - e^{\frac{\rho^2 \cdot s}{50}} \cdot \left(1 - erf\left(\rho \cdot \sqrt{\frac{s}{50}}\right)\right) + \left[x \cdot \left(\frac{2 \cdot S_1}{\sqrt{\pi}} + \frac{\sqrt{50} \cdot R_1}{\rho}\right) + \sum_{i=1}^{s-1} \left[\Psi_i \cdot \left(\frac{2 \cdot S_{s-i+1}}{\sqrt{\pi}} + \frac{\sqrt{50} \cdot R_{s-i+1}}{\rho}\right)\right]\right] \cdot \frac{1}{\sqrt{50}}\right]^2\right], x\right]$

$p := \frac{t}{d \cdot 50} .. \frac{\Delta E}{dE} + \frac{t}{d \cdot 50} - 1 \quad potencijal_p := Es - \left(p - \frac{t}{d \cdot 50}\right) \cdot dE \quad \Psi c_p := \Psi_{(p+1) \cdot 50} \quad \Psi a_p := \Psi_{50 \cdot p + 25}$

$= I(2FSCL)^{-1}(Df)^{-1/2}$



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